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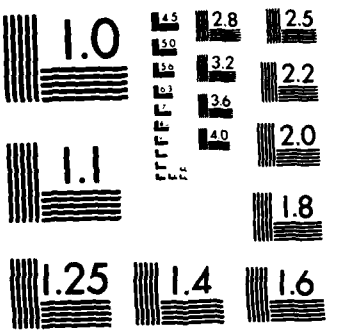

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ORIGINAL

COMPUTER CORRECTION

OF

RESISTANCE ERRORS IN POLARIZATION DATA

by

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ABSTRACT

RESIST, a short microcomputer program, detects and corrects resistance (IR) errors in cathodic polarization data. It requires a minute or less to calculate the corrosion rate, the cathodic Tafel constant, and the resistance.

INTRODUCTION

Considerable corrosion research has centered on the relationship between the potential and applied current at a polarized electrode. This relationship is used to determine corrosion rates, electrode kinetics constants, and cathodic protection requirements. Ideally, the reference electrode in a polarization experiment should be positioned very close to the working electrode. If it is not, a voltage drop (viz. IR error) may occur due to the current in the electrolyte between the reference and working electrodes. This becomes critical, if the IR error is large and of comparable magnitude to the electrode potential.

In the past, several approaches have been employed to minimize or eliminate IR effects[1]. For electrolytes with low to moderate resistivity, it can be appreciably reduced by placing a Luggin-Haber probe very near the working electrode. Unfortunately, this approach is not useful for electrolytes with high resistivity (e.g., water). There are other methods, which compensate the error instrumentally. These include positive feedback compensation techniques[2], and Wheatstone bridge circuits[3]. In this investigation, a different approach has been adopted by treating the uncompensated polarization data, instead of correcting the IR error during the experiment. The simplest example of this occurs when the value of R is known. Hence, the IR error can be calculated and subtracted from the measured polarized potentials. However, R is usually unknown. In such cases, numerical methods (i.e. computer calculations) may be used. A microcomputer program, RESIST, which utilizes an exponential regression analysis has been developed to accomplish this goal.

APPROACH

A cathodically polarized corroding metal follows the following relationships[4], if IR error is present:

$$IA = IC(10^{-P/BC} - 10^{P/BA}) \quad (1)$$

and

$$P = PT - (IA)R \quad (2)$$

where IA is the applied current; IC is the corrosion current; BA and BC are the anodic and cathodic Tafel constants; R is the effective resistance between the reference and the electrodes of the electrolyte; P is the activation overpotential; and PT is the total overpotential equal to (E-EC) where EC is the corrosion potential and E is the polarized potential. Due to the nature of equation (1), algebraic calculation of the electrochemical parameters is not possible. Graphical or numerical methods must be used.

A short program, BETACRUNCH[5], was developed earlier to solve equation (1) in the absence of IR effects. Here, we employ a different approach which may be used to analyze cathodic polarization data containing IR errors. At high cathodic overpotentials, the second term in equation (1) becomes negligible, hence:

$$IA = IC(10^{-P/BC}) \quad (3)$$

Equations (2) and (3) form the basis for this method. The procedure is: a) assume a value of R and correct the measured potentials using equation (2); b) Perform an exponential regression analysis on equation (1) using these corrected potentials and the measured current values to obtain values for BC, IC and the cooefficient of correlation; c) Repeat these steps with other values of R to find the one which yields the highest coefficient of correlation. Although these calculations are

straightforward, they are very time-consuming. A simple, short computer program, RESIST, which rapidly executes these calculations, is described below.

PROGRAM DESCRIPTION

RESIST is listed in Table 1. The program line functions and the variable names are described in Appendix A. The general features of the program are as follows:

1. It accepts cathodic polarization data obtained from systems under activation or diffusion control. A minimum of 3 data points is required.
2. It calculates the resistance, R, between the reference and working electrodes; the corrosion current, IC; and the cathodic Tafel constant, BC.
3. It can run on any Basic language microcomputer with a minimum of 2K memory.*
4. It is rapid. Typically, it requires less than a minute to obtain the results.

The command 'RUN' initiates the program. The program requests the user to input the corrosion potential and the polarization data. The analysis begins after this input is completed. Although only 3 data points is necessary for the analysis; best results are obtained by entering numerous points. The units of the final resistance obtained depend on units of the potential and applied current input data (e.g., if potential and current are expressed in mV and ma, then resistance is expressed in ohms.). Resistance is calculated to the nearest 0.0001; resistances less than this are given as zero.

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*RESIST is written for the Apple Computer (Apple Computer Inc., Cupertino, CA.) However, it may be easily modified for other Basic microcomputers.

In general, RESIST should be run using data obtained at high overvoltage values, usually greater than -250 mV where equation (3) is valid. Unfortunately, at very high overpotentials concentration polarization and/or other reduction processes (e.g. water decomposition) may occur. If this occurs, BC will vary and equation (3) will be invalid. The problem of knowing whether the overpotential range selected is correct may be determined by analysing another data set at an adjacent or overlapping potential range and comparing the results. The influence of insufficient overpotential and/or concentration polarization can safely be assumed to be negligible if the two data sets yield the same result. Here, we call this the "double check" technique.

RESULTS

RESIST has been tested using both generated and experimental data. Equations (1) and (2) and extended polarization equations (4) were used to generate data.

Table 2 shows some generated data, representing a system under activation and concentration polarization with resistance. Analyses of these results by RESIST are listed in Table 3. The double check technique, discussed above, was used at low, medium, and high overpotentials. The results are very similar for the medium overpotential ranges, but differ at low and high overpotentials. Note that the results calculated at medium overpotentials differ from, but are very close to those used to generate the data.

Table 3, shows that by using the double check technique, it is possible to select an optimum overpotential range for data analysis. For low limiting diffusion currents (e.g. those close to the corrosion

current), it might not be possible to find an optimum range. However, this would be detected by the double check technique.

Table 4 illustrates the results of analyzing a diffusion-controlled system (large BC value). The value of IC is in good agreement with that used to generate the data. Although there is some error in the magnitude of BC, it is relatively unimportant. However, the error in the calculated value of R is large and the coefficient of correlation is low. This is the result of the extreme slope of the polarization curve.

Jones[7] used a Wheatstone bridge circuit to directly compensate for IR errors during polarization measurements with 3004 Aluminum in water. Simultaneously, he also measured the uncompensated potentials. Thus, a comparison between his direct method and the results obtained by RESIST is possible. This is shown in Table 5. Jones calculated BC and IC from his compensated data by conventional, graphical Tafel extrapolation[4].

Apart from a slight discrepency in the resistance value, there is good agreement between the two methods. The double check technique could not be adopted in this example due to unavailability of more data points at higher overpotential values.

APPLICATIONS

RESIST may be used to compensate for IR errors in cathodic polarization data obtained in a variety of corroding systems. The best results are achieved by analyzing many data points obtained from activation-controlled systems (low BC values) with high limiting diffusion currents (moderate to high concentration of the reducible species). A unique advantage of RESIST is that previously obtained polarization data may be examined for IR errors.

LIMITATIONS

The program limitations are imposed by the nature of equations (2) and (3) which form the basis of the method. An implicit assumption in equation (3) is that the second term in equation (1) may be neglected (viz. the data points are obtained at high overpotentials.). It also assumes that BC is constant. If a second reduction process, or concentration polarization commences within the potential range of interest, then BC will vary, and erroneous results may be obtained. As shown here, it is possible to find a suitable range for analysis by the double check technique. Note that problems only arise if BC varies. Hence, systems under complete diffusion control may be analyzed, although somewhat imperfectly (Table 4).

RESIST is a powerful program - it is capable of affecting major corrections to experimental data. However, it always yields results, which, in some cases, may be incorrect. Table 3 shows several examples. Note that the coefficient of correlation may be very close to one even though the calculated parameters are incorrect. For these reasons, the program should be used with great care. The double check method should be employed to verify the accuracy of the program output. It may not be possible to analyze some systems because of insufficient data or concentration polarization effects.

ACKNOWLEDGMENT

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```
1  REM

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          RESIST
 IR ERROR CORRECTION PROGRAM
  R.H. GANDHI & N.D. GREENE
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=============================

INPUT/SET R STEP

10  HOME : DIM P(30),E(30),IA(30),IB(3
    0):MF = 0: INPUT "DATA PTS. = ";N
    : INPUT "ECORR = ";EC: PRINT : FOR
    I = 1 TO N: INPUT "E,I = ";E(I),I
    A(I):IB(I) = IA(I): NEXT
20 C = 1: READ RS:RE = RS: GOSUB 100: IF
    B < 0 THEN 20
30  IF RS <  = 10 THEN  READ RS:C = 2:
    RE = 0:UR = 100:CR = 0: GOTO 100
40 MF = MF + 1: FOR I = 1 TO N:IB(I) =
    (10 ^ MF) * IA(I): NEXT : RESTORE
    : GOTO 20
50 CR = 0:UR = RF + RS: IF RS > 1 AND
    B < 0 THEN UR = RE
60 RE = RF - RS: READ RS: IF RS = 0 THEN
    RE = RF
70  IF RE < 0 OR (RE < 5 AND RS > .05)
     THEN RE =  - RS
80 RE = RE + RS: IF RE > UR THEN 50
90  DATA   100,50,10,5,1,.5,.1,.05,.01
    ,.005,.001,.0005,.0001,0: REM

REGRESSION ANALYSIS

100 J = 0:K = 0:L = 0:M = 0:R2 = 0: FOR
    I = 1 TO N:P(I) = EC - E(I) - IB(
    I) * RE: IF P(I) < 0 THEN B =  -
    1: GOTO 120
110 X = P(I):Y =  LOG (IB(I)):J = J +
    X:K = K + Y:L = L + X ^ 2:M = M +
    Y ^ 2:R2 = R2 + X * Y: NEXT :B =
    (N * R2 - K * J) / (N * L - J ^ 2
    ):IC =  EXP ((K - B * J) / N):J =
    B * (R2 - J * K / N):M = M - K ^
    2 / N:K = M - J:CC =  SQR (J / M)

120  IF RS = 0 THEN 170
130  IF C = 1 THEN  RETURN
140  IF B < 0 THEN 50
150  IF CC > CR THEN CR = CC:RF = RE
160  GOTO 80: REM

PRINT RESULTS

170  PRINT : PRINT : PRINT "RESISTANCE
     = ";RE * (10 ^ MF): PRINT "IC =
    ";IC * (10 ^  - MF): PRINT "BC =
    "; INT (23030 / B + .5) / 10000: PRINT
    : PRINT "COEFF. OF CORRELATION =
    ";CC
```

Table 2

GENERATED POLARIZATION DATA OF SYSTEM UNDER
ACTIVATION AND CONCENTRATION POLARIZATION WITH IR ERROR

PARAMETERS ARE:

EC = 0; IC = 10: BC = 120: BA = 100: R = 1: IL = 1000

DATA NO.	POTENTIAL	CURRENT	DATA NO.	POTENTIAL	CURRENT
1	-14.23	4.17	13	-252.30	120.65
2	-28.48	8.37	14	-288.41	146.38
3	-42.94	12.77	15	-330.02	177.51
4	-57.79	17.56	16	-378.30	215.19
5	-73.24	22.94	17	-434.69	260.82
6	-89.49	29.11	18	-500.94	316.07
7	-106.79	36.32	19	-579.18	382.99
8	-125.42	44.83	20	-672.05	464.06
9	-145.70	54.98	21	-782.85	562.26
10	-168.02	67.13	22	-915.88	681.23
11	-192.84	81.75	23	-1077.71	825.35
12	-220.71	99.37	24	-1369.76	999.96

(NOTE: IL IS THE LIMITING DIFFUSION CURRENT.)

Table 3

ANALYSIS OF GENERATED DATA AT DIFFERENT OVERPOTENTIAL RANGES

RESULTS

DATA NOS.	OVERPOTENTIAL RANGE	IC	BC	R	COEFF. OF CORRELATION
3-6	low	4.58	39.2	1.99	0.999923526
5-8	low	6.41	74.3	1.40	0.999992372
12-15	medium	9.43	116.4	1.02	1.00000043
14-17	medium	9.63	117.7	1.02	1.00000012
20-23	high	0.30	52.7	1.09	0.997386095
21-24	high	276.45	2392.4	0.00	0.981998233

(NOTE - DATA NOS. CORRESPOND TO DATA IN TABLE 2)

Table 4

PROGRAM PRINTOUT OF RESULTS OBTAINED USING GENERATED DATA
(EC = 0; IC = 50; BC = 10E+06; BA = 60; AND R = 3)
EXECUTION TIME = 35 SECONDS

DATA PTS. = 4
ECORR. = 0

E, I = -349.99,50
E, I = -360.03,50.01
E, I = -370.04,50.01
E, I = -380.06,50.02

RESISTANCE = .2998
IC = 49.8007375
BC = 192249.014

COEFF. OF CORRELATION = .777386305

Table 5

COMPARISON OF RESULTS CALCULATED BY RESIST PROGRAM AND MEASURED DIRECTLY BY JONES (REFERENCE NO. 7) (CATHODIC POLARIZATION OF 3004 ALUMINUM IN WATER.)

UNCOMPENSATED DATA OBTAINED BY JONES AND USED FOR ANALYSIS:*

CORROSION POTENTIAL	DATA NO.	POTENTIAL IN VOLTS	APPLIED CURRENT IN AMPERES
-0.975 V	1	-2.4397	0.001
	2	-1.3815	0.0002
	3	-1.2087	0.0001
	4	-1.1223	0.00005

	RESULTS OBTAINED BY:	
ELECTROCHEMICAL PARAMETERS	RESIST (CALCULATED)	JONES (DIRECT)
Resistance, R (in ohms).	1209.2	1100
Tafel constant, BC (in volts)	0.134	0.135
Corrosion current, IC (in amps.)	1.24E-05	1.04E-05

*These data were received as a separate communication from D. A. Jones.

APPENDIX A

RESIST - PROGRAM DETAILS

LINE FUNCTIONS

The purpose of the program lines (refer to Table 1) are briefly described below:

LINE 10, 20: Dimension and input statements.

LINES 30 to 50: Determines the initial resistance increment value.

LINES 60 to 90: Determines the values of resistance increment and the lower and upper limits of resistance for further analysis.

LINE 100: Data statement containing various resistance increment values, RS.

LINES 110 to 160: Perform the exponential regression analysis* on the equation shown below,

$$IA = IC(10^{P/BC})$$

LINE 170: Checks if resistance increment is zero, which indicates the end of analysis and goes to line 220.

LINE 180: Checks the value of a flag, initialized in line 30, which is used to execute a Return statement.

LINE 190: Checks if the value of variable B is negative, which indicates the resistance value is too large.

LINE 200: Tests for the largest value of the coefficient of correlation and stores it in variable CR. Also the corresponding resistance is saved in variable RF.

---

*This subroutine is used essentially as listed in reference No. 6.

LINE 210: Returns to line 60 for another set of analysis.

LINE 220: Prints final results.

RESIST - PROGRAM VARIABLE NAMES

N - Number of data values.

EC - Corrosion potential.

MF - Multiplying factor used to multiply applied current values (line 50) and store in Array IB.

Array IA - Stores N applied current values.

Array IB - Stores N potential values

Array P - Stores N overpotential values.

RE - Resistance value.

UR - Upper limit of resistance to be analysed.

RS - Resistance increment value.

IC - Corrosion current.

CC - Coefficient of correlation.

CR - Variable used to store the highest value of the coefficient of correlation, CC.

B, J, K, L, M, R2, X, Y - Variables used in exponential regression analysis routine (lines 110 to 160).

C - Variable used as flag in lines 30 and 180. Flag value changed in line 40.